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DEVELOPMENT OF REFRIGERATING OIL FOR HFC-134a ROTARY COMPRESSOR

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ABSTRACT

This paper reports the investigation of new refrigerating oil for the rotary compressors with HFC-134a in place of CFC-12. In the first investigation, we evaluated synthetic polyalkylene glycols (PAGs) oils, but these oils led to some serious problems such as capillary tube blockage with sludge and severe wear at sliding surface. In order to solve those problems, several oils, whether they are soluble or insoluble in HFC-134a, are investigated by using of the sealed glass tube test, the wear test and the life test using actual refrigerators. As the result of these investigations, we have chosen a very low viscous alkyl benzene oil. The HFC-134a rotary compressor for household refrigerator with selected oil has exhibited more reliability than that of previous CFC-12 rotary compressors.

INTRODUCTION

Since CFCs contain some ozone-depleting chlorines, they must be replaced by HCFCs or HFCs by the end of 1995. HFC-134a having no ozone-depleting chlorine is the leading candidate to replace CFC12, because its thermodynamic properties are relatively close to those of CFC-12. However, HFC134a is insoluble in current refrigerating oils for CFC-12 compressors such as parafinic and naphtenic mineral oils. Immiscibility causes serious problems in refrigeration systems because oils can not return to the compressor.

Polyalkylene glycols (PAGs), which are soluble in HFC-134a, were evaluated in our first investigation. But it was difficult for the refrigerators using PAGs to obtain the same reliability as current CFC-12 ones, because PAGs cause two problems such as capillary tube blockage with sludge and severe wear at the sliding surface between the vane and the rolling piston in the rotary compressors.

In order to solve those problems, synthetic polyol ester oils and alkyl benzene oils have been investigated in terms of their chemical stability and lubricity and these oils have been also evaluated by using the actual refrigerators under accelerating conditions.

EXPERIMENTAL

Three kinds of ester oils (ESTER-a,ESTER-A1,and ESTER-A2) and four kinds of branched alkyl benzene oils (BAB-b,BAB-c,BAB-B,and BAB-C) were used in this study. Hereafter small letters, a,b and c, mean that those oils do not contain any additives, and capital letters, A,B and C, show that they have some additives. The viscosity of BAB-c is higher than that of BAB-b. The physical properties of the investigated oils are summarized in Table 1. HFC134a is commercially available, and its purity was 99.99%.

Thermal and Chemical stability of the oils was studied by a sealed glass tube method (Fig.1). The sealed glass tube tests (S.G.T.T.) are also used in order to study the influence of contaminated water on the chemical stability of the oils. These tests were performed at 175℃ for 14 days. After the pre-selected periods, the tubes were opened for the following evaluation. The refrigerants were analyzed by a gas chromatography-mass spectrometer (GC-MS,Shimadzu, Model OX-1000EX), and the decomposition of the oils was evaluated by the optical spectra of the oils.

Oxidative stability of the oils and the effectiveness of anti-oxidation additives were studied by the chemilluminescence analyzer (TOHOKU DENSI SANGYOU, Model CLD100, Fig.2). The exothermic bimolecular reaction of peroxy radical is known to produce ketones in the excited triplet state.[1] Ketones in the triplet state falls to the ground state emitting visible light. This process is called "chemilluminescence(CL)". The chemilluminescence analyzer has often been used to investigate the oxidative reaction rate of many polymers.[2]

Lubricity was investigated by a wear tester. By using this apparatus, it is possible to perform the wear test under the same conditions as those in the actual rotary compressor except for the method of oil supply to the sliding surface between the vane and the rolling piston. The test conditions are shown in Table 2. The failure loads were measured by the pin and V-blocks wear tester (MAX-WIELAND).

The life tests using actual refrigerators was performed under acceleration conditions. The temperature in the refrigerators were always monitored through the test. The refrigerators were disassembled and inspected at the completion of the test sequence. The refrigerants were analyzed by GC-MS. The decomposition of the refrigerating oils were evaluated by measuring the total acid number. Furthermore the small amounts of the compounds formed through the decomposition of the oils were analyzed by GC-MS. The sludge which adhered to the wall of capillary tubes were analyzed by micro FT-IR and EPMA.

RESULT AND DISCUSSION

The results of the sealed glass tube and the wear tests are summarized in Table 3. It was shown that all of the investigated oils without water have good chemical stability . On the contrary, the ester oils , which are contaminated with water above 0.5% by weight, showed poor chemical stability. Alkyl benzene oils showed excellent chemical stability even under the condition of water contaminating above 1.0% by weight . HFC134a showed excellent chemical stability under all conditions.

Branched alkyl benzene oils showed good lubricity by the wear tester. Small amounts of the wear of the vane occurred in branched alkyl benzene oils whether or not anti-wear additives were contained. When ester oils did not contain anti-wear additives, the significant amounts of the wear occurred. But the wear decreased with increasing the activity of anti-wear additives. The wear in Ester-A2, which contained more active anti-wear additives than those contained in Ester-A1, decrease by three times as less as the wear in alkyl benzene oils. The test results of measuring the failure loads by using the pin and V-block wear tester showed that ester oils have good lubricity whether or not the anti-wear additives were contained. When alkyl benzene oils contained anti-wear additives, their failure loads were the same as ester oils. But alkyl benzene oils which did not contain anti-wear additives, their failure loads became a half of ester oils.

The results of the oxidation tests by the chemilluminescence analyzer are shown in Fig. 3 . The rates of the oxidation were in the order of ESTER-a > BAB-c = BAB-d . The rate of oxidative reaction of the ester base oil is faster than that of the alkyl benzene base oils. Since there are many difficulties to perfectly remove oxygen gas in the refrigeration cycle, oils have to prevented from oxidation. The effectiveness of an anti-oxidation additive is shown in Fig.4. It has been made clear that the anti-oxidation additive is effective at 150℃ in the concentration of less than 0.03wt% .

The results of the life tests are summarized in Table 4. The refrigerators with ESTER-A1 failed the life tests in terms of the capillary tube blockage with the formed sludge. It has been shown by FT-IR that the sludge primarily consists of esters and metallic soaps. It is considered that the esters in the sludge are polymerized, because the full width at half maximum (FWHM) of C=O stretching band around $1740cm^{-1}$ is broader than that of the ester oil. The decomposition products in the oils were identified by GC-MS analysis to be fatty acids generated by hydrolysis of the ester. The acid number increased to 0.26mgKOH/gr because of the increased fatty acids in the oils. The significant amounts of the vane and the rolling piston wears occurred in Ester-A1. In order to solve this problem, several special materials for the sliding parts were examined, but the wear was not able to be improved.

When the ordinary materials were used for the sliding parts, the refrigerators with ESTER-A2 were not able to pass all of the life tests because of severe wear generation at sliding parts. The refrigerators with ESTER-A2 reached the final of the life tests by making use of special materials for the sliding parts , although fairly amounts of the sludge were observed on the wall of the capillary tube. The sludge primarily consisted of the iron salts of phosphoric acid and small amounts of the polymerized products of ester oil as well as metallic soaps. The decomposition products in the oils are shown to consist of small amounts of fatty acids and fairy amounts of cresols by GC-MS analysis. It has been considered that cresols were generated by the reaction of the anti-wear additives with the iron surface[3] of the vane and the rolling piston. The increase in the acid number of oils were less than that in ESTER-A1.

It is considered that since anti-wear additives do not exhibit the effectiveness in the polar oils, the ester oil needs much activities to the anti-wear additives in order to form the boundary layer on the sliding surfaces. The formed boundary layer by the anti-wear additives prevents the ester oils from the adsorption on the iron surfaces. Since the polymerization of oil has been considered to occur on metal surfaces, the degradation of ESTER-A2 on the iron surfaces are less than those of ESTER-A1[4],[5].

The refrigerators with BAB-B completed all of the life tests and only trace amounts of sludge adhered to the capillary tube. It has been shown by FT-IR that the sludge primarily consisted of the decomposed additives and the polymerized or oxidation products were not observed. The analytical results of the oils showed that increase of acid number was slight and the decomposition products of the oil were not detectable by GC-MS analysis. It is considered that since the adsorptive activities of alkyl benzene oils are much lower than that of ester oils, the activities of alkyl benzene oils are much lower than that of ester oils on the iron surfaces. On the other hand, anti-wear additives react easily with iron[2] and only these additives become the sludge in alkyl benzene oils. The vane wear was much smaller than that of ester oils. Alkyl benzene oils did not require the special materials for the sliding parts. Although the boundary layer formed from the reacting chlorine with iron surfaces has been reported to decrease wear at sliding surfaces [6], alkyl benzene oils exhibit excellent lubricity even without chlorine. It has been considered that alkyl benzene oils are not diluted by refrigerant, and the extreme pressure additives have much effect in nonpolar oils. In order to make clear the reason for decreasing wear, further investigations of the microscopic characteristics of the lubrication will be needed .

The refrigerators with BAB-C failed the life test, because the temperature in the refrigerator increased. The temperature increase was caused by increasing thermal resistance in the evaporator, because oil covered the inner surface of the evaporator.

CONCLUSION

In order to select the refrigerating oil for HFC-134a rotary compressor, we investigated several oils whether they are soluble or insoluble in HFC-134a.

The life tests by actual refrigerators with ester oils showed that ester oils require the special materials for the sliding surface and the active anti-wear additives in order to obtain the same reliability as the CFC-12 refrigerators. The results of the sealed glass tube test showed that the ester oils need strictly control of the contaminated water concentration. On the other hand, it is easy for low viscous alkyl benzene oils to exhibit the same reliability as the CFC-12 refrigerators, because alkyl benzene oils have excellent lubricity even without boundary layer formed chlorine and they have good chemical stability.

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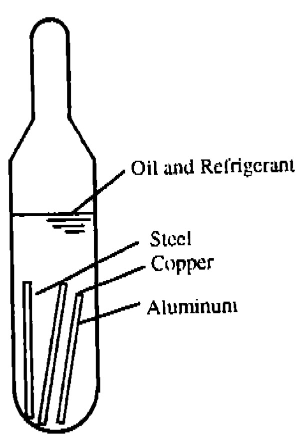

FIG 1 Experimental arrangement of sealed glass tube

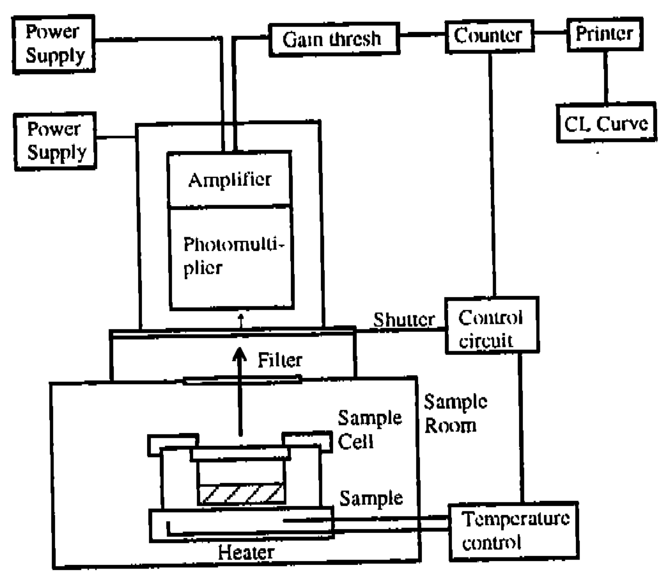

FIG 2 Schematic diagram of chemilluminescence analyzer

Table 1 Physical properties of the oils

Item \ Oil	ESTER-a	ESTER-A1	ESTER-A2	BAB-b	BAB-B	BAB-c	BAB-C
Materials	Synthetic ester (hindered)	Ester-a +A.W. +A.O.	Ester-a +A.W. +A.O.	Branched alkyl benzene	BAB-b +A.W. +A.O.	Branched alkyl benzene	BAB-c +A.W. +A.O.
Color (ASTM)	L0.5			L0.5		L0.5	
Viscosity	Base			Lower than ESTER-a		Same as ESTER-a	
Solbulity U-CST (℃) L-CST (℃)	>80 -48			– –		– –	
Total Acid Number (mgKOH/g)	<0.01			0.00		0.00	
VolumeRegistance (Ω·cm)	4.8×10^{13}			$>10^{15}$		$>10^{15}$	
Density (g/cm^3 @15℃)	0.9630			0.867		0.867	
Pour Point (℃)	-47.5			<-50		-42.5	

A.W. : Anti Wear additives
A.O. : Anti Oxidation additives
U-CST : Upper-Critical Solution Temperature
L-CST : Lower--Critical Solution Temperature

Table 2 The wear test condition

	Real refrigerators	Wear tester
Contact Configration	vane/rolling piston	vane/rolling piston
Atmosphere	gaseous refrigerant	gaseous refrigerant
Load / line	0.4kg/mm	1~5kg/mm
Sliding speed	-0.6~0.7m/sec.	0.2~2m/sec.
Oil temperature	80~160℃	R.T~150℃

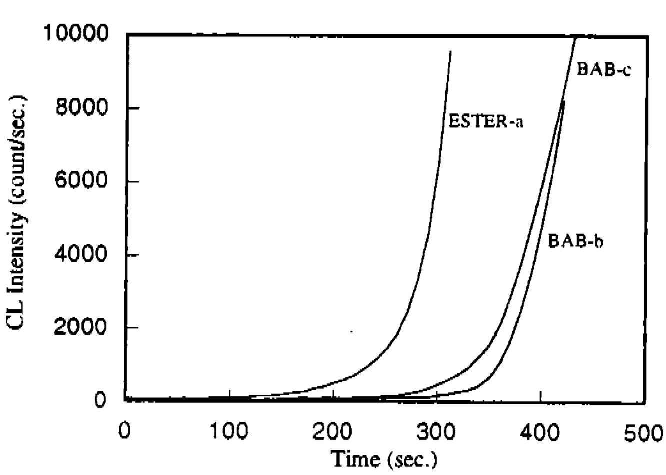

FIG 3 Chemilluminescence intensities in various resrigerating oils

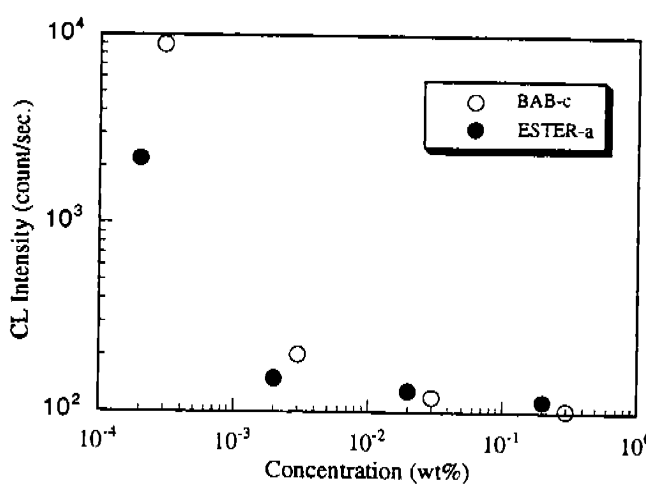

FIG 4 Effect of addition of anti oxidative additives of chemilluminescence intensity

Table 3 The test result of the various refrigerating oils

Item / Oils	Additive	SGTT: Contaminant	SGTT: Transmittance	SGTT: Refrigerant's purity	wear test: Wear volume	wear test: Failure load
ESTER-a	none	none water 0.5wt% water 1.0wt%	95.0% 38.0% 32.0%	>99.9 >99.9 >99.9	249×10^{-4}mm^2	○
ESTER-A1	A.W. A.O.	none	95.5%	>99.9	62×10^{-4}	○
ESTER-A2	A.W. A.O.	none	95.0%	>99.9	45×10^{-4}	◎
BAB-b	none	none water 0.5wt% water 1.0wt%	99.0% 91.3% 89.0%	>99.9 >99.9 >99.9	14×10^{4}	×
BAB-B	A.W. A.O.	none	96.3%	>99.9	14×10^{4}	◎
BAB-c	none	none water 0.5wt% water 1.0wt%	98.5% 92.3% 91.0%	>99.9 >99.9 >99.9	9.5×10^{4}	×
BAB-C	E.P. A.O.	none	97.5	>99.9	9.2×10^{4}	◎

A.W. : Anti Wear additive

A.O. : Anti Oxidation additive

Table 4 The typical test result of the refrigerating oil by using the actual refrigerator

Item / Oils	Discharge temperature (℃)	Operating time (hr)	Wearing amounts of vane (μm)	Sludges	Principal constituent of the sludges	Purity of the refrigerant	Color of oil (ASTM)	Total acid number (mgKOH/g)	Reliability / Results
ESTER-A1	120	1000	151	Fairly ~Trace	metallic soap polymerized oil	99.96	2.0	0.20	Failed / poor cooling faculty
	140	1000	90	Heavy	↑	99.90	3.0	0.26	Failed / poor cooling faculty
ESTER-A2	120	1000	56	None	decomposited additives	99.95	1.0	0.06	Failed / severe wear at sliding surface
	140*	9000	35	Fairly	↑	99.95	1.0	0.07	Completed / OK
BAB-B	120	1000	10	None	↑	99.95	0.5	0.01	Completed / OK
	140	9000	15	Trace	↑	99.95	0.5	0.03	Completed / OK
BAB-C	120	1000	10	Trace	↑	99.95	0.5	0.01	Failed / cooling faculty down

* : Special materials were used for the sliding parts.